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Ceramic Integration Technologies for Advanced Energy Systems: *Critical Needs, Technical Challenges, and Opportunities*

Abstract

Advanced ceramic integration technologies dramatically impact the energy landscape due to wide scale application of ceramics in all aspects of alternative energy production, storage, distribution, conservation, and efficiency. Examples include fuel cells, thermoelectrics, photovoltaics, gas turbine propulsion systems, distribution and transmission systems based on superconductors, nuclear power generation and waste disposal. Ceramic integration technologies play a key role in fabrication and manufacturing of large and complex shaped parts with multifunctional properties. However, the development of robust and reliable integrated systems with optimum performance requires the understanding of many thermochemical and thermomechanical factors, particularly for high temperature applications.

In this presentation, various needs, challenges, and opportunities in design, fabrication, and testing of integrated similar (ceramic-ceramic) and dissimilar (ceramic-metal) material systems have been discussed. Experimental results for bonding and integration of SiC based Micro-Electro-Mechanical-Systems (MEMS) LDI fuel injector and advanced ceramics and composites for gas turbine applications are presented.

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Ceramic Integration Technologies for Advanced Energy Systems

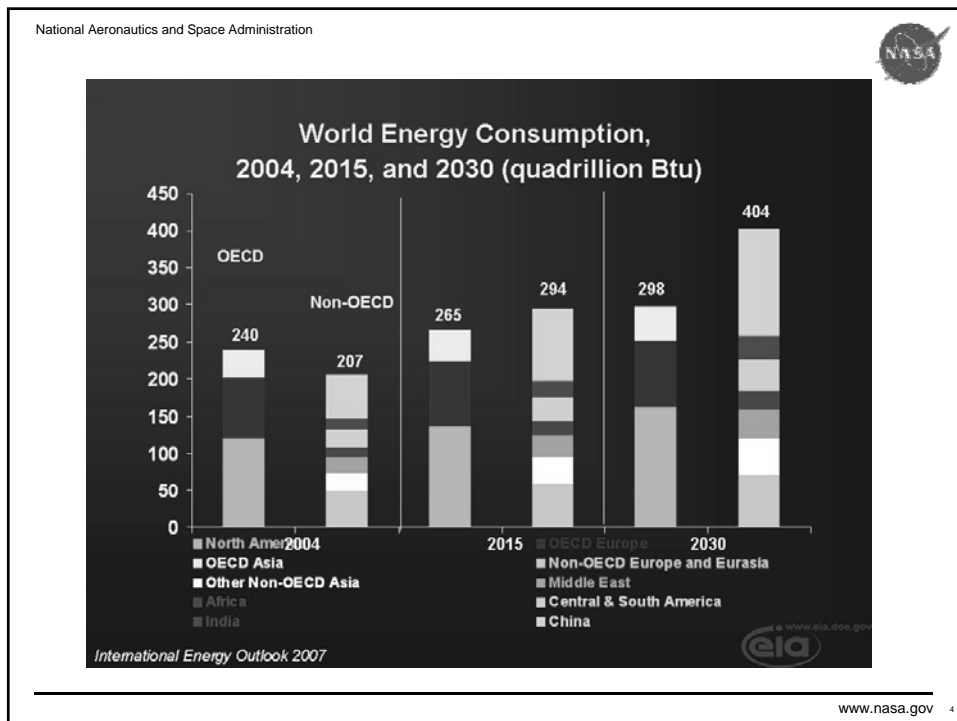
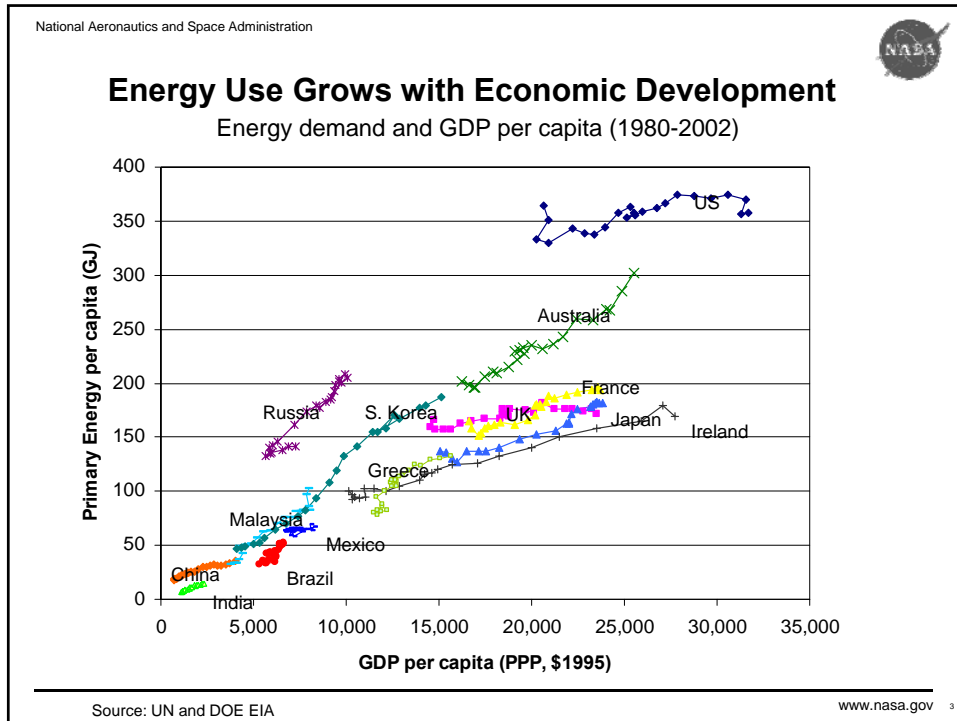
Critical Needs, Technical Challenges, and Opportunities

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NASA Glenn Research Center
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Overview

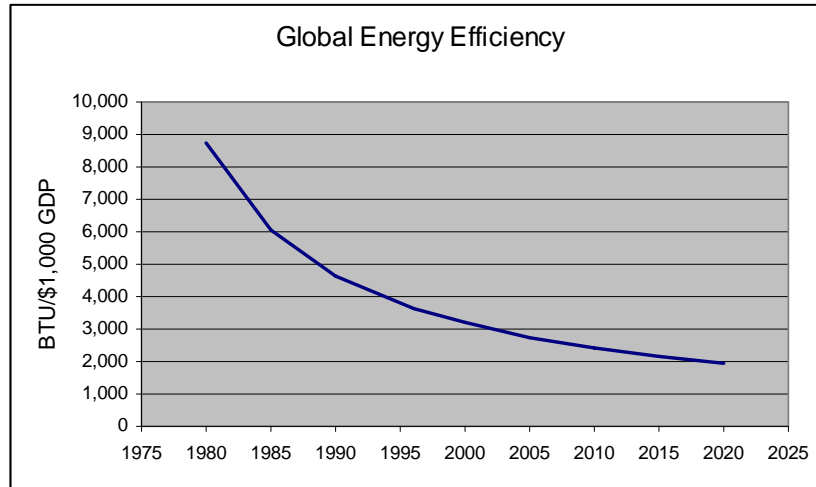
- **Introduction and Background**
 - *Global Energy Issues and Role of Ceramics*
- **Technical Challenges in Integration**
 - *Similar vs Dissimilar Systems*
 - *Role of Interfaces*
 - *Thermal Expansion Mismatch and Residual Stresses*
 - *Design and Testing*
- **Ceramic Integration Technologies**
 - *Improved Efficiency and Low Emissions:*
 - *Gas Turbine Components*
 - *MEMS-LDI Fuel Injector*
 - *Thermal Management Systems*
 - *Heat Exchangers and Recuperators*
 - *Alternative Energy Systems*
- **Concluding Remarks**



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Advanced Materials and Technologies Play a Key Role in Improving Energy Efficiency



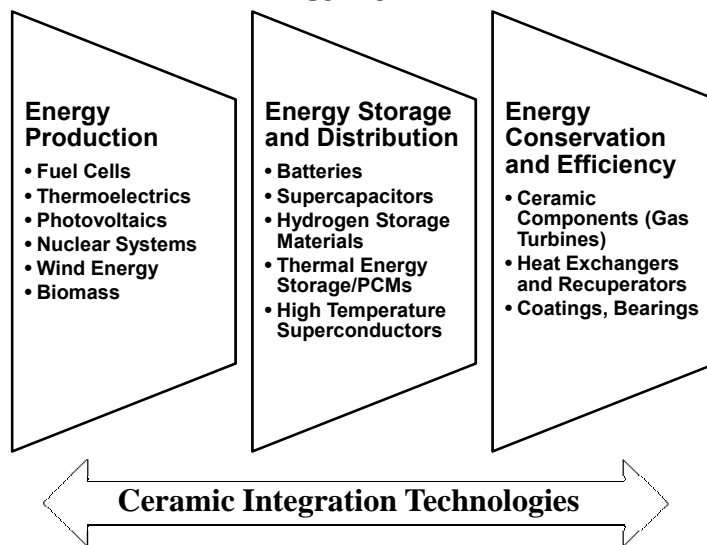
Source: Millennium Project, 2020 Global Energy Delphi Round 2

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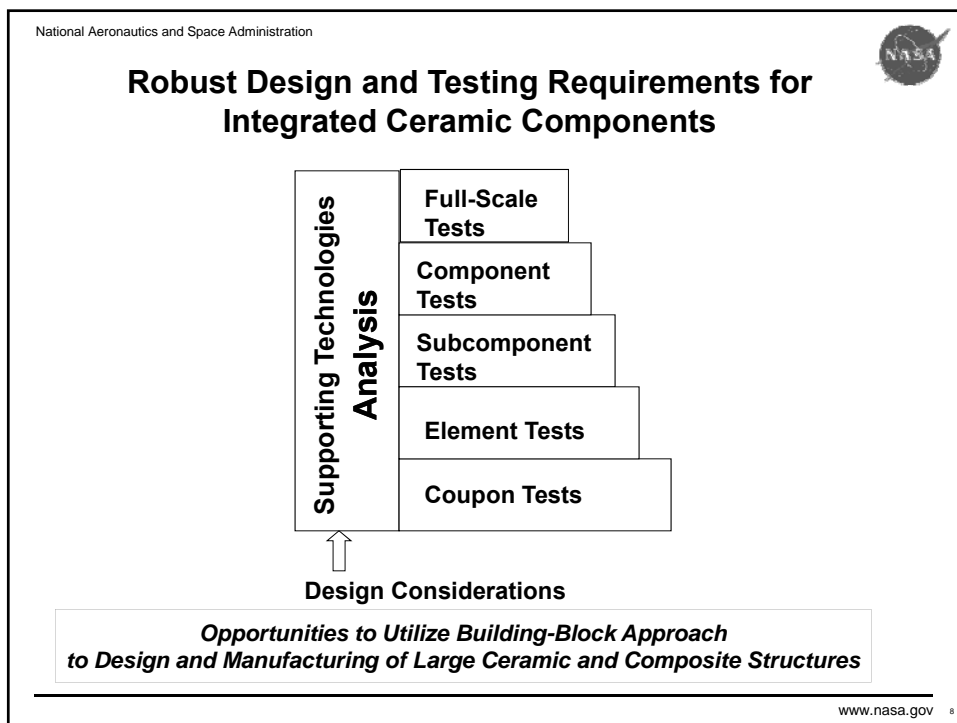
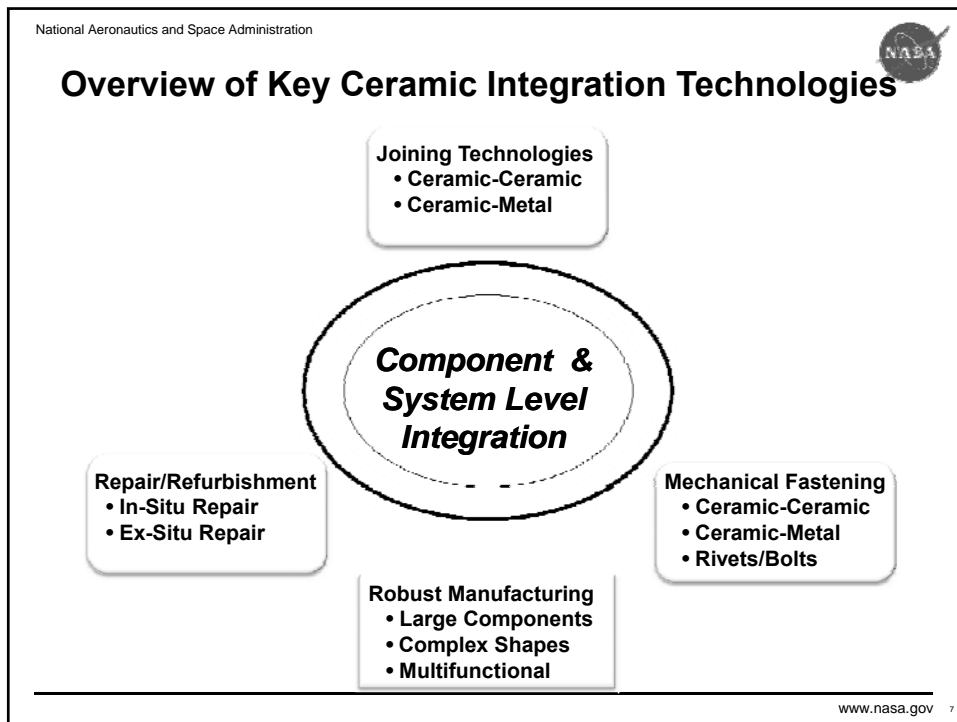
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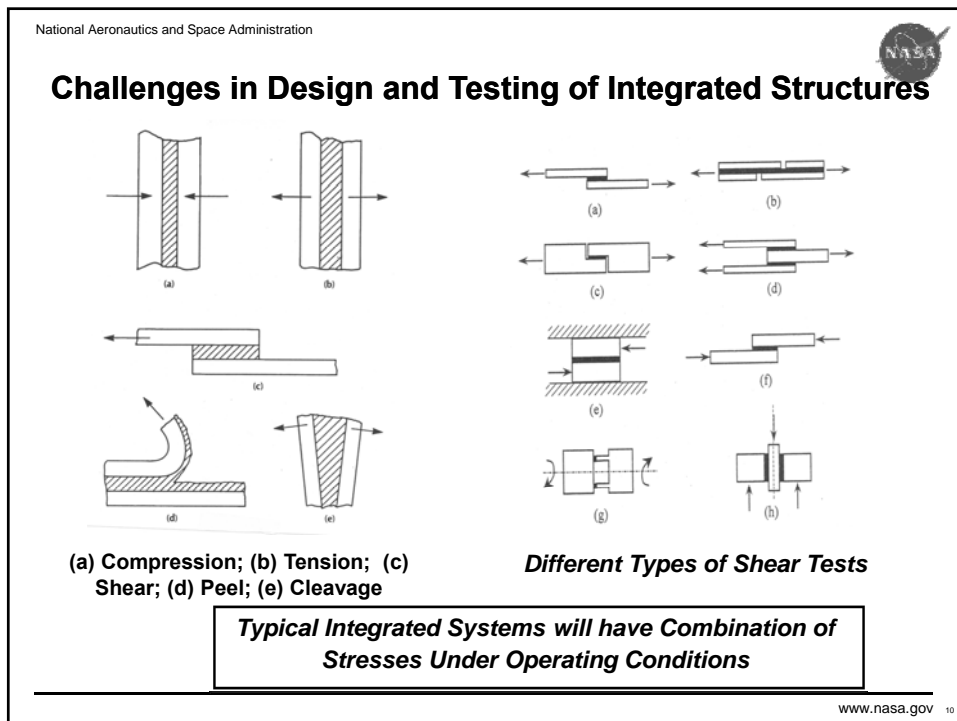
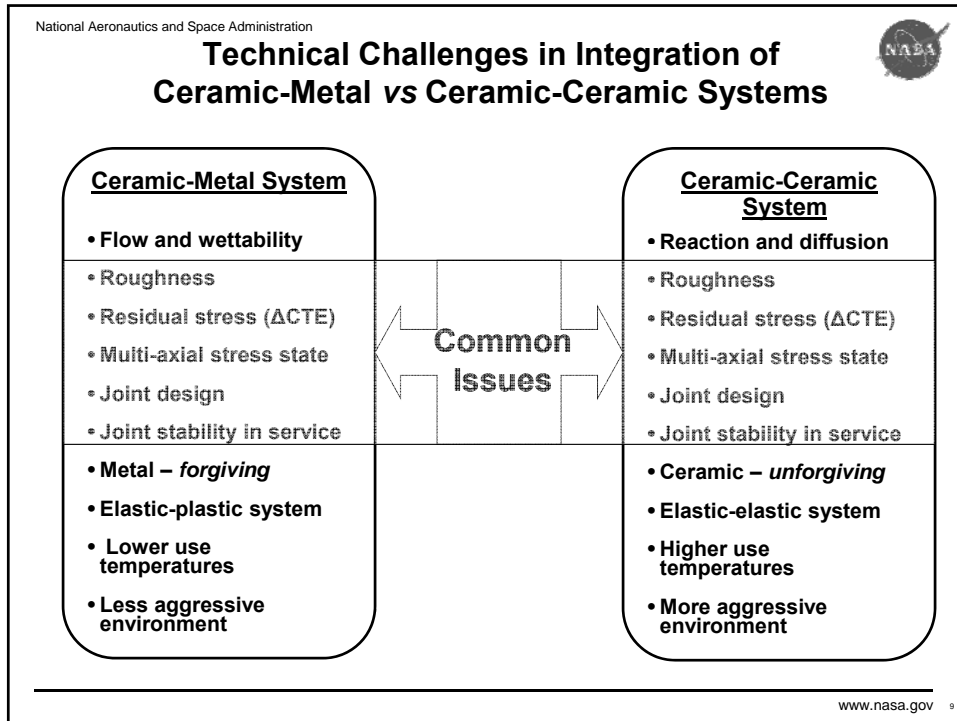


Critical Role of Advanced Ceramic Technologies in Energy Systems



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Wetting and Interfacial Phenomena in Ceramic-Metal System

Key Challenges:

- **Poor Wettability of Ceramics and Composites:**
(poor flow and spreading characteristics)
- **Surface Roughness and Porosity of Ceramic Substrates**
- **Thermoelastic Incompatibility**

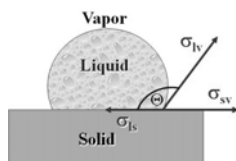
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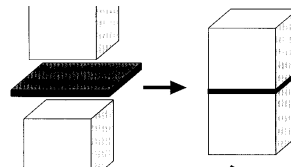


Wettability is Important Factor in Brazing

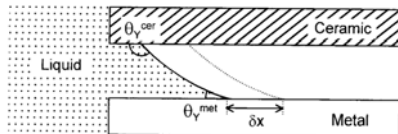
Young's equation
 $\sigma_{sv} - \sigma_{sl} = \sigma_{lv} \cos \theta$



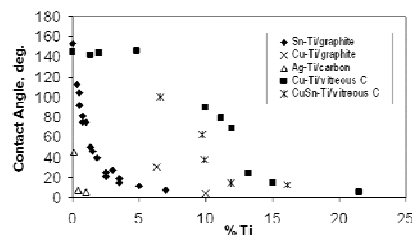
Contact angle of braze should be small



Braze layer melts and spreads between the substrates to form the joint

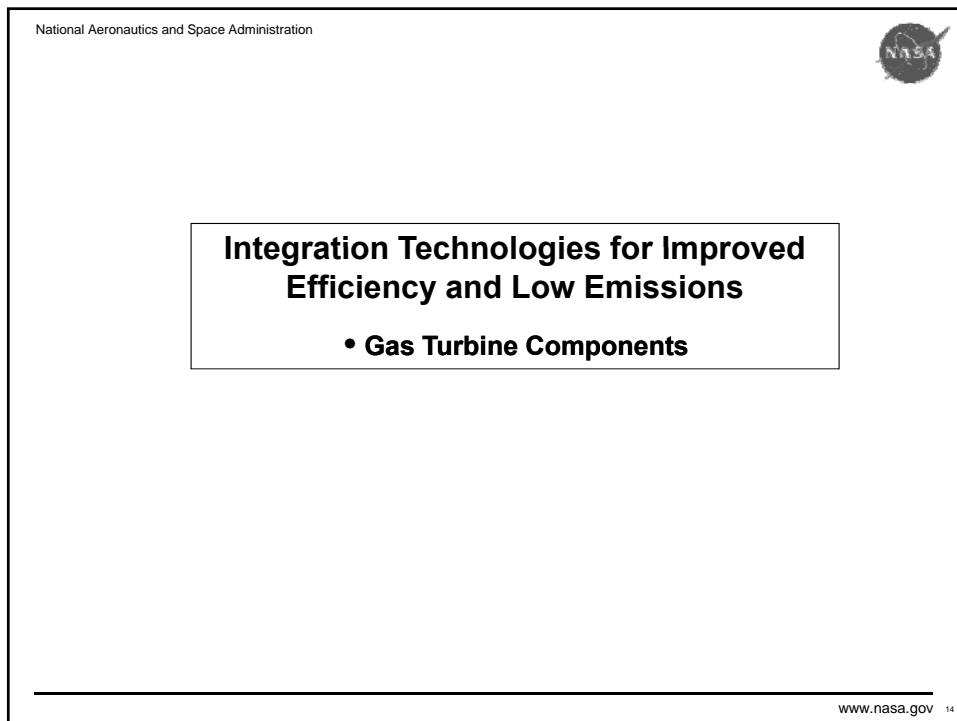
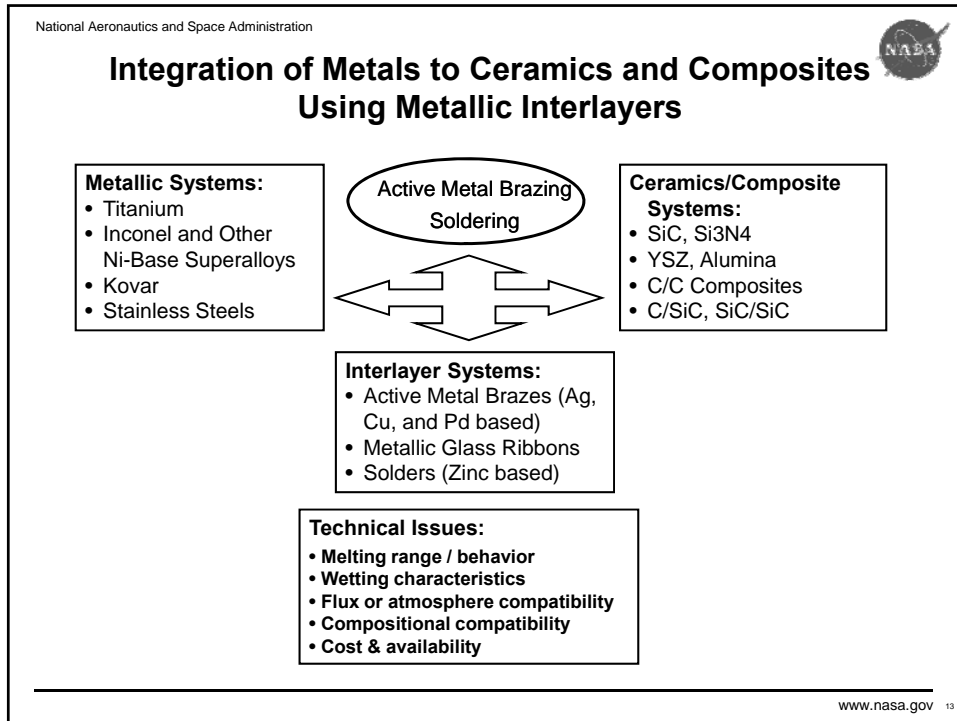


Ordinary braze alloys wet the metal but not the ceramic systems



Must use 'active' brazes that wet and bond with both metal and ceramics

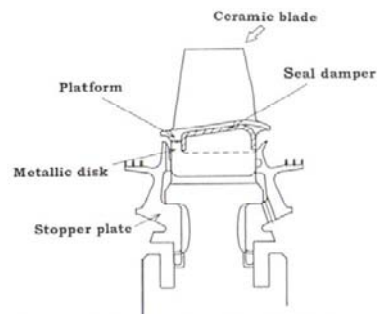
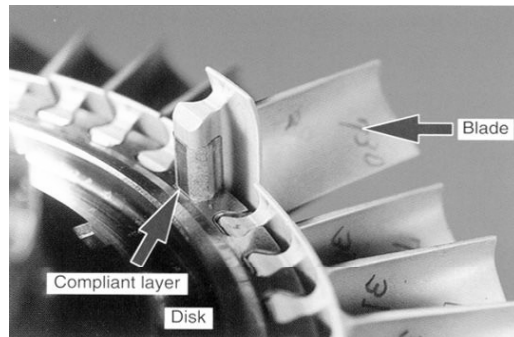
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Advanced Silicon Nitride Based Components for Propulsion Systems



Hybrid Gas Turbine Blade (Ceramic Blade and Metallic Disk)
in NEDO's Ceramic Gas Turbine R&D Program, Japan (1988-1999)

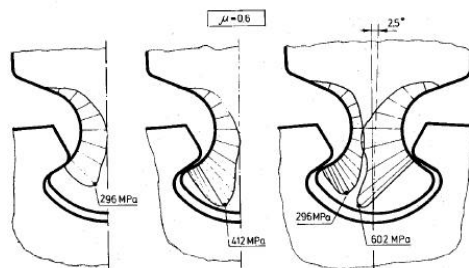
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Integration Technologies for Silicon Nitride Ceramics to Metallic Components

Issues with Ceramic Inserted Blades



There are contact stresses at the metal-ceramic interface. Compliant layers (i.e. Ni-alloy+Pt) are used to mitigate the stress and damage. Failures can occur in the compliant layer.

Mark van Roode, "Advances in the Development of Silicon Nitride and Other Materials", Environmental Barrier Coatings Workshop, November 6, 2002, Nashville, TN.

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Integration Technologies for Silicon Nitride Ceramics to Metallic Components

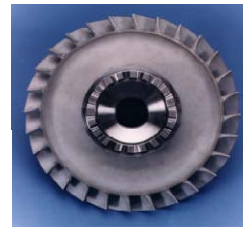
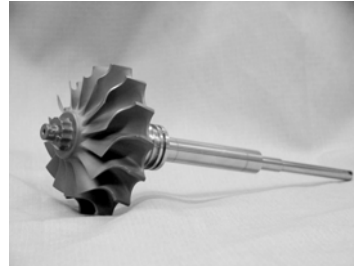
INTEGRAL ROTORS

- No Compliant Layer with Disk
- Attachment of Ceramic Rotor to Metal Shaft
- Primarily Small Parts
- Ability to Fabricate Larger Parts Has Improved
- Integral Rotors are Replacing Metal Disks with Inserted Blades



Mark van Roode, Solar Turbines

Industry Direction



IR Silicon Nitride Rotor,
DOE Microturbine
Program (top)
H-T. Lin, ORNL

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Integration of Silicon Nitride to Metallic Systems

Approach: Use multilayers to reduce the strain energy more effectively than single layers.

Challenge: Multiple interlayers increase the number of interfaces, thus increasing the probability of interfacial defects.

Material	CTE $\times 10^6/K$	Yield Strength, MPa
Silicon nitride	3.3	-
Inconel 625	13.1	-
Ta	6.5	170
Mo	4.8	500
Ni	13.4	14-35
Nb	7.1	105
Kovar	5.5-6.2	270
W	4.5	550

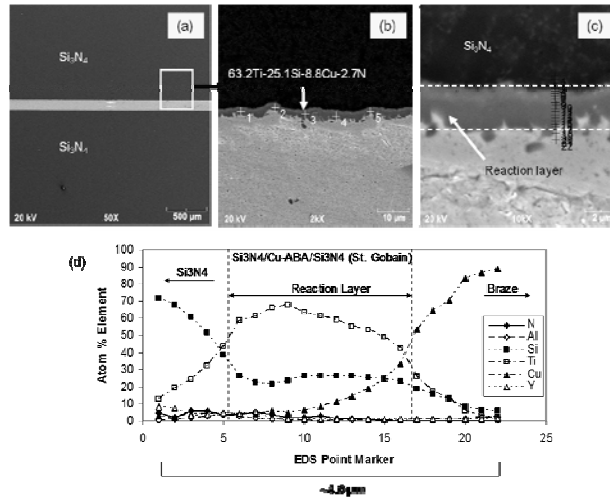
Various combinations of Ta, Mo, Ni, Nb, W and Kovar to integrate Silicon nitride to Nickel-Base Superalloys

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Microstructure of Silicon Nitride Joints Using Cu-ABA (92.75Cu-3Si-2Al-2.25Ti) Interlayers



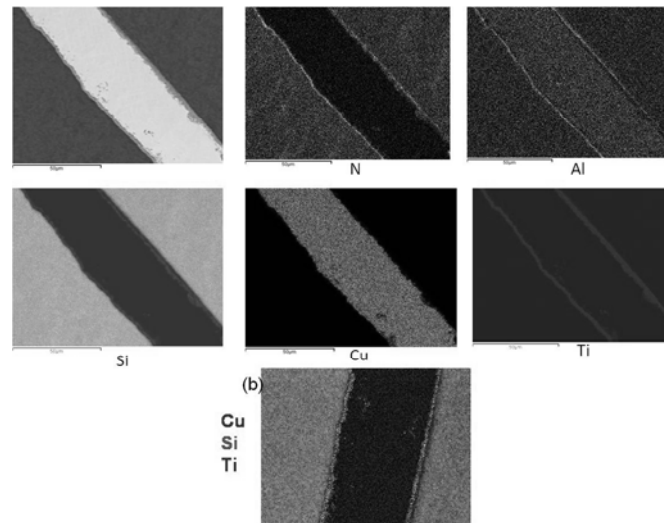
M. Singh, R. Asthana, F.M. Varela, J.M. Fernandez, J. Eur. Ceram. Soc. (2010) in press

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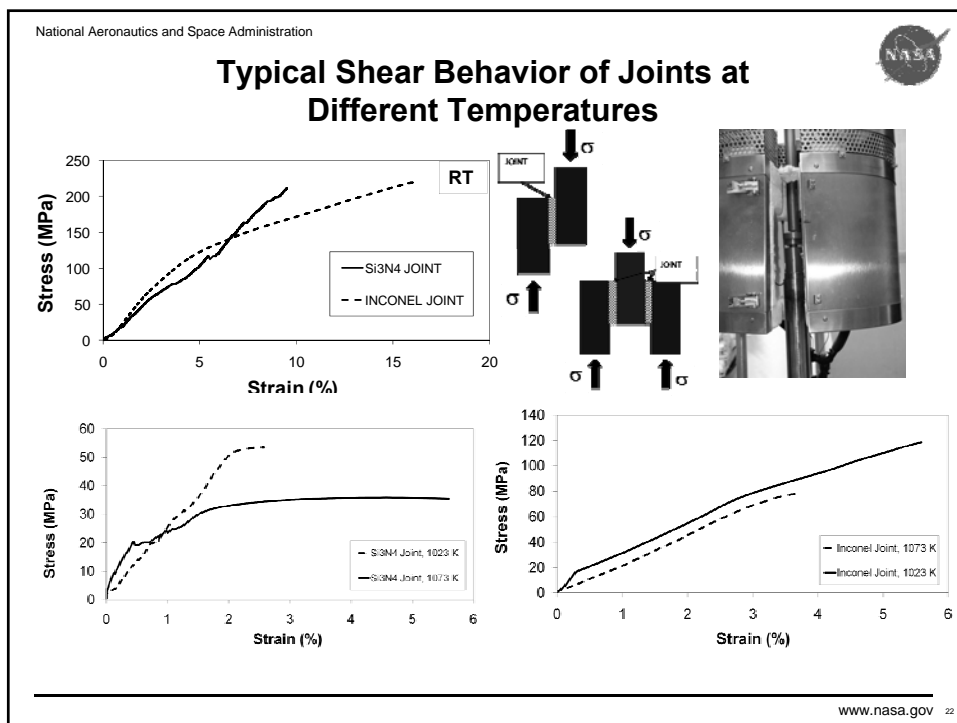
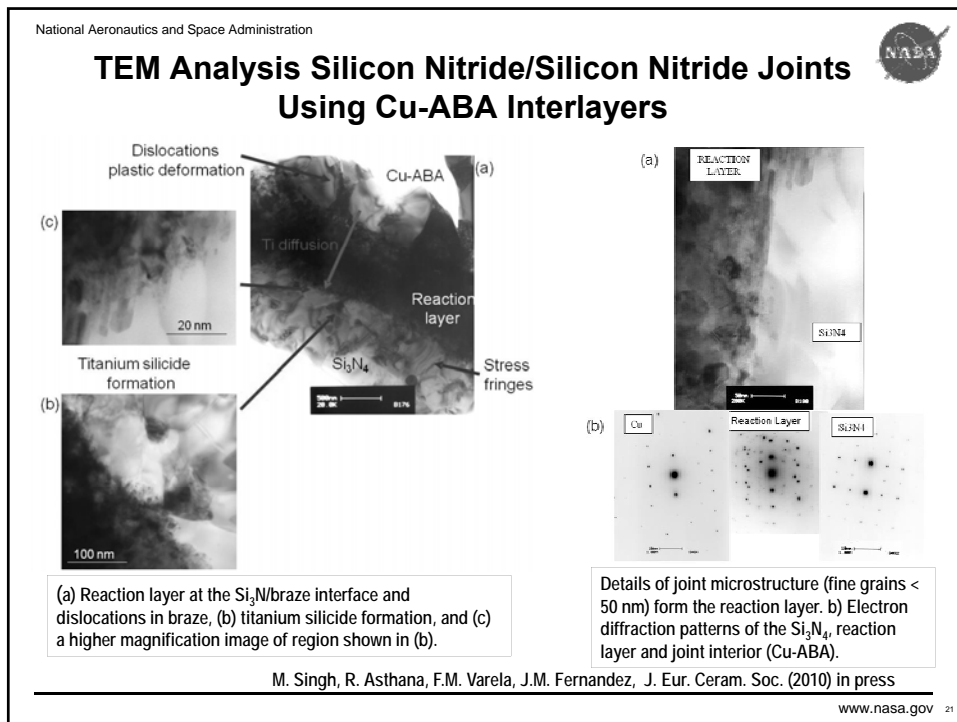


EDS Compositional Maps of Silicon Nitride/Silicon Nitride Joints Using Cu-ABA Interlayers



Titanium Segregation at the Interface

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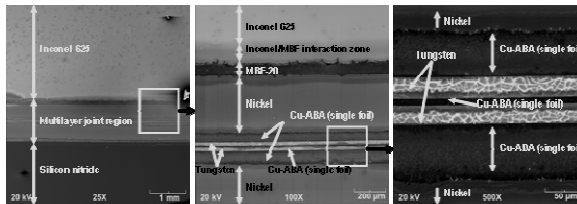
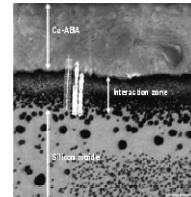
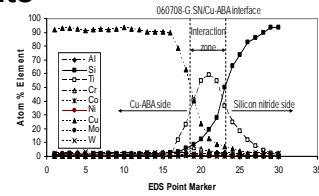
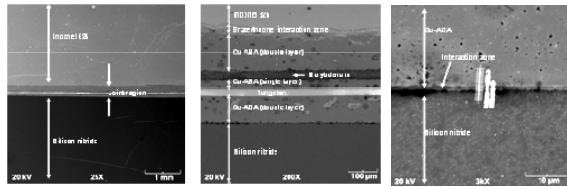


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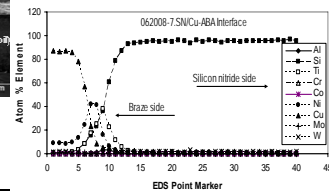
Microstructure of Silicon Nitride/Inconel 625 Multilayer Joints



$\text{Si}_3\text{N}_4/\text{W}/\text{Mo}/\text{Inconel 625}$ (Cu-ABA, brazed at 1044C, 30 min.).



$\text{Si}_3\text{N}_4/\text{Ni}/\text{W}/\text{Ni}/\text{Inconel 625}$
(with Cu-ABA on SN side and MBF on Inconel side)
(brazed at 1044C, 30 min.).



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Integration Technologies for Improved Efficiency and Low Emissions

- MEMS-LDI Fuel Injector

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Integration Technologies for MEMS-LDI Fuel Injector

Objective: Develop Technology for a SiC Smart Integrated Multi-Point Lean Direct Injector (SiC SIMP-LDI)

- Operability at all engine operating conditions
- Reduce NOx emissions by 90% over 1996 ICAO standard
- Allow for integration of high frequency fuel actuators and sensors

Possible Injector Approaches

1. Lean Pre-Mixed Pre-Evaporated (LPP)

Advantages - Produces the most uniform temperature distribution and lowest possible NOx emissions

Disadvantages - Cannot be used in high pressure ratio aircraft due to auto-ignition and flashback

2. Lean Direct Injector (LDI)

Advantages - Does not have the problems of LPP (auto-ignition and flashback)

- Provides extremely rapid mixing of the fuel and air before combustion occurs

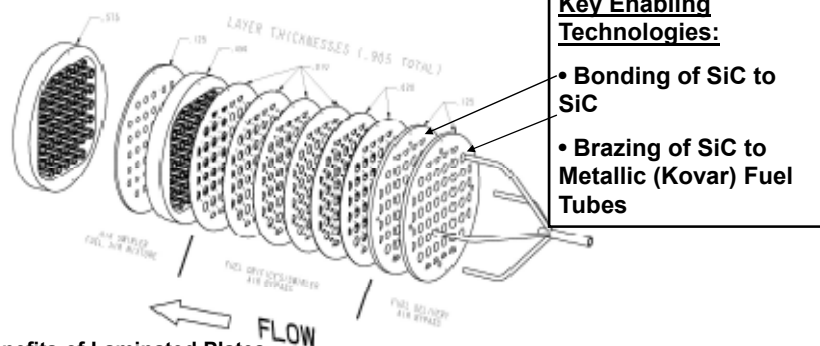
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Lean Direct Injector Fabricated by Bonding of SiC Laminates

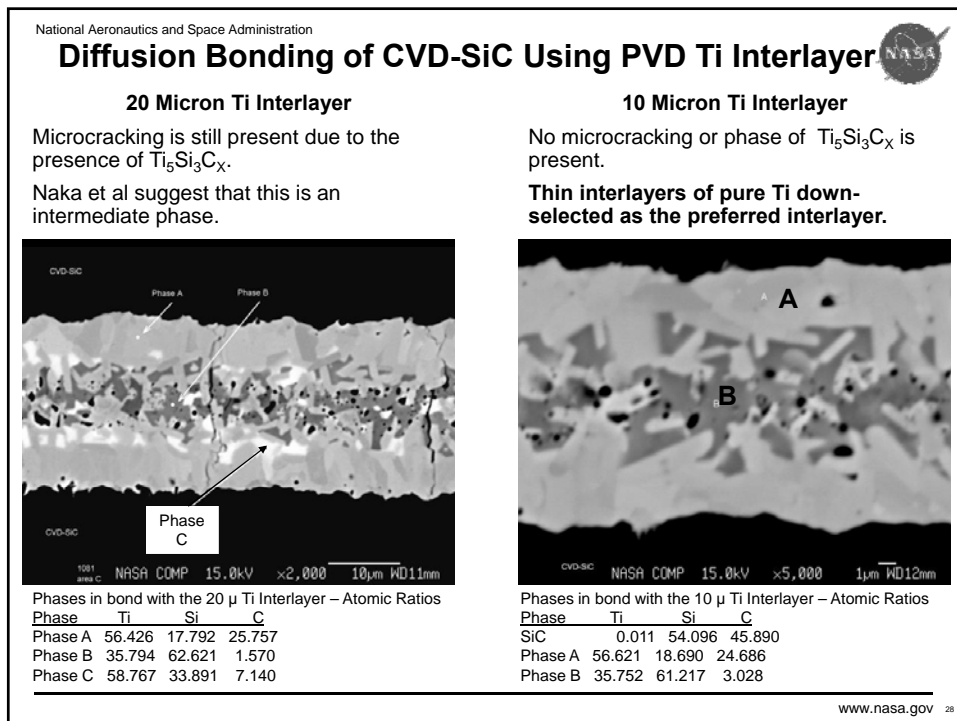
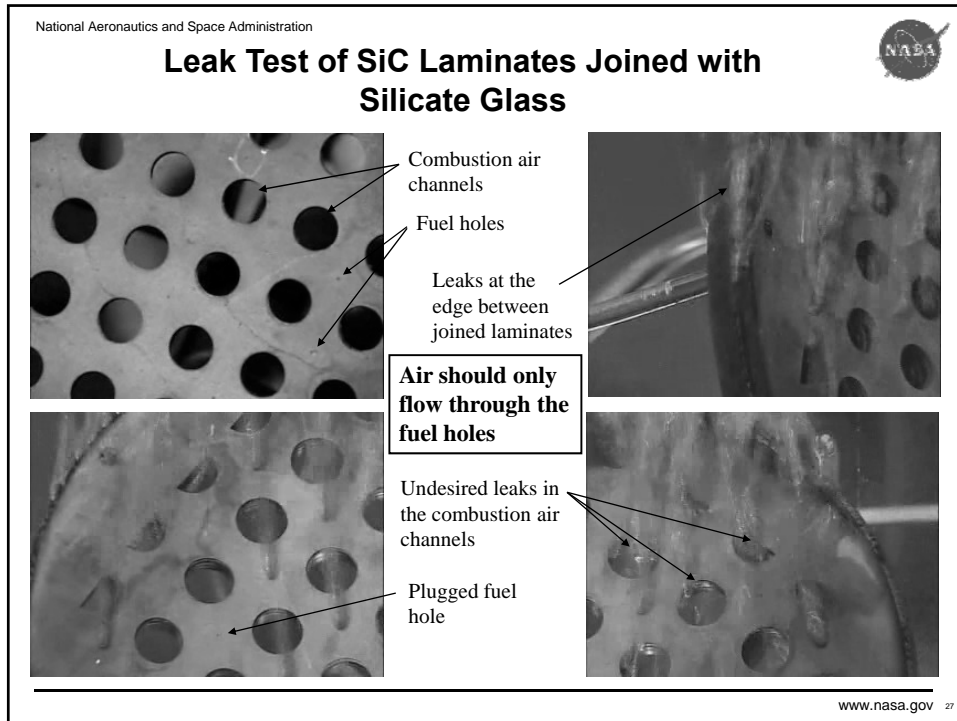
SiC laminates can be used to create intricate and interlaced passages to speed up fuel-air mixing to allow lean-burning, ultra-low emissions

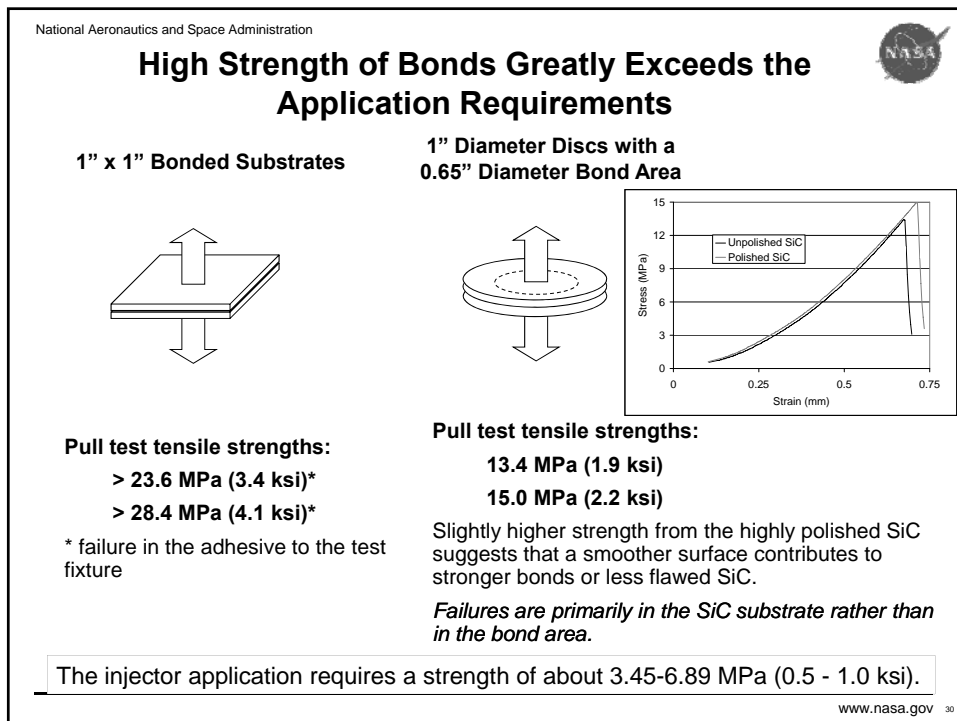
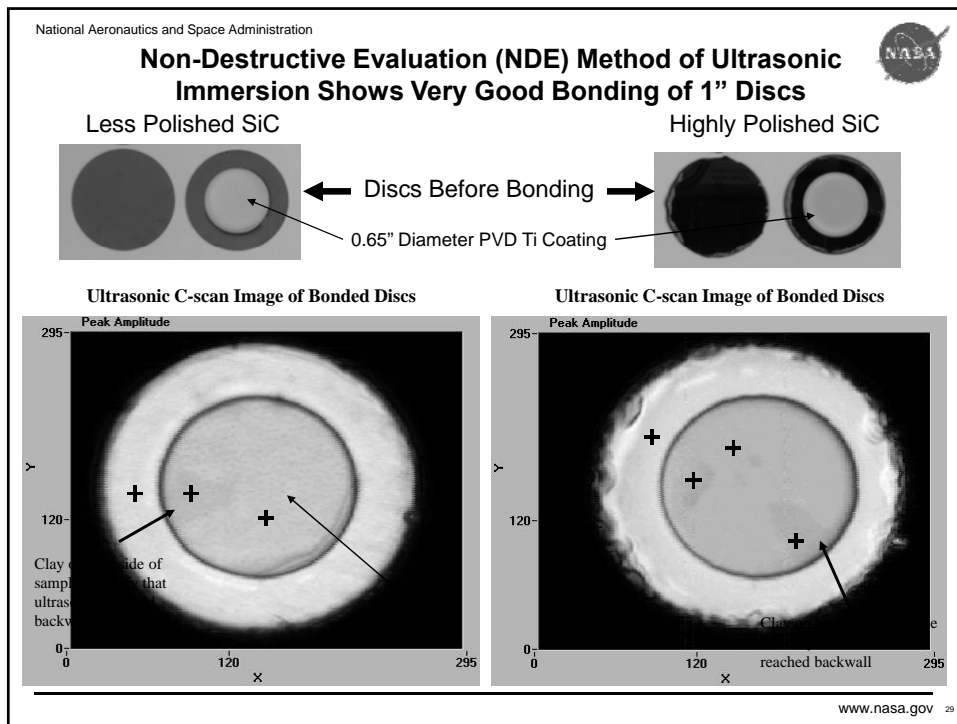


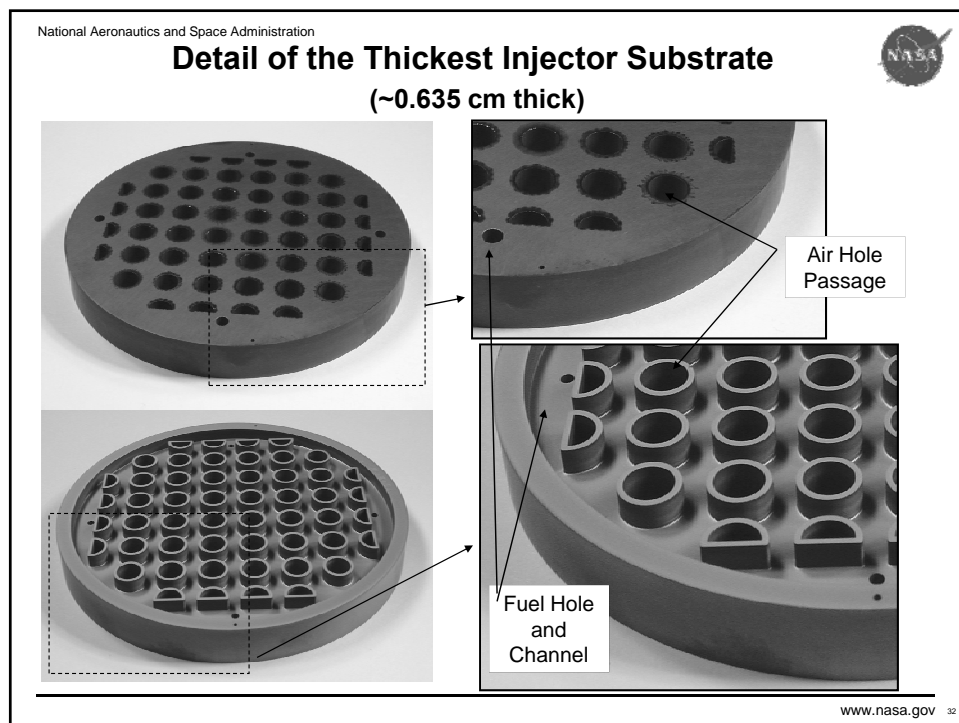
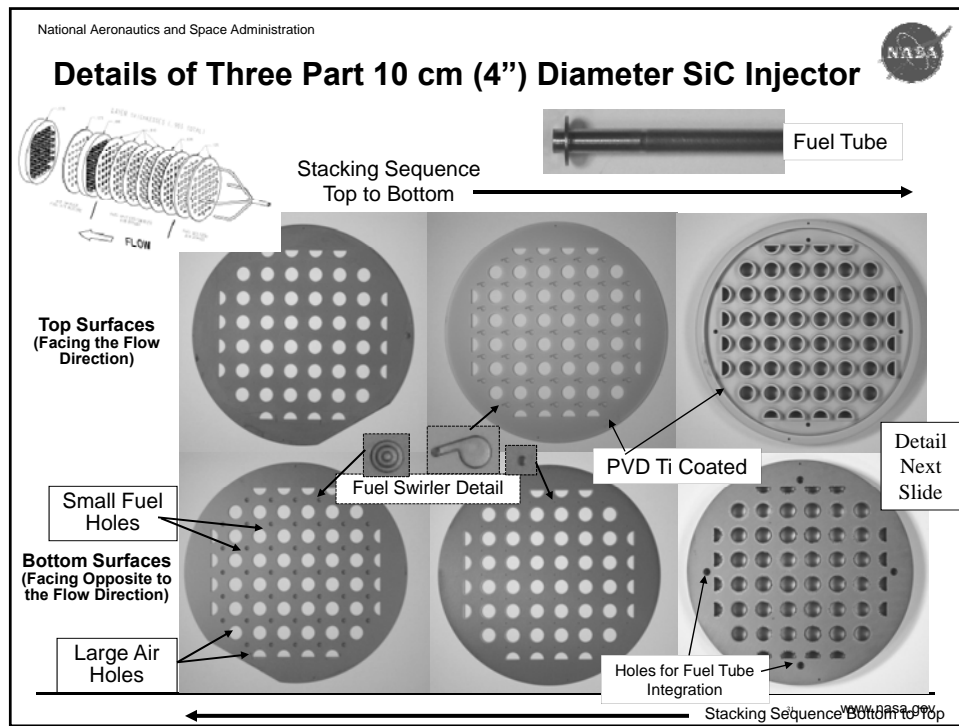
Benefits of Laminated Plates

- Passages of any shape can be created to allow for multiple fuel circuits
- Provides thermal protection of the fuel to prevent choking
- Low cost fabrication of modules with complicated internal geometries through chemical etching

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Integration Technologies for Improved Efficiency and Thermal Energy Storage Devices

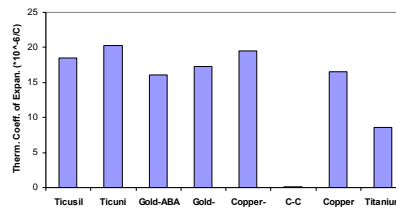
- Thermal Management Systems
- Heat Exchangers/Recuperators
- Thermal Energy Storage



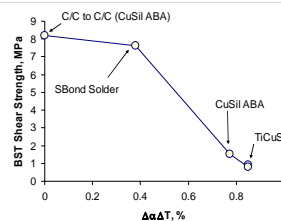
Bonding of Titanium to C/C Composites

- We had joined C-C composite to Ti tubes for lightweight heat exchanger applications.
- Both direct bonding using braze layers and indirect bonding using a porous carbon foam (saddle material) and braze layers were employed.
- Excellent bonding of active braze to foam, C-C Composite, and Ti Tube occurred.
- Failure always occurred in Poco HTC (Saddle Material) indicating that bond strength exceeded the fracture strength of foam.

1. *M. Singh et al, Mater. Sci. Eng. A (498, 1-2 (2008) 31-36.*
2. *M. Singh et al, Mater. Sci. Eng., A 412, 2005, 123-128.*
3. *G.N. Morscher et al, Mater. Sci. Eng., A 418(1-2), 2006, pp 19-24.*

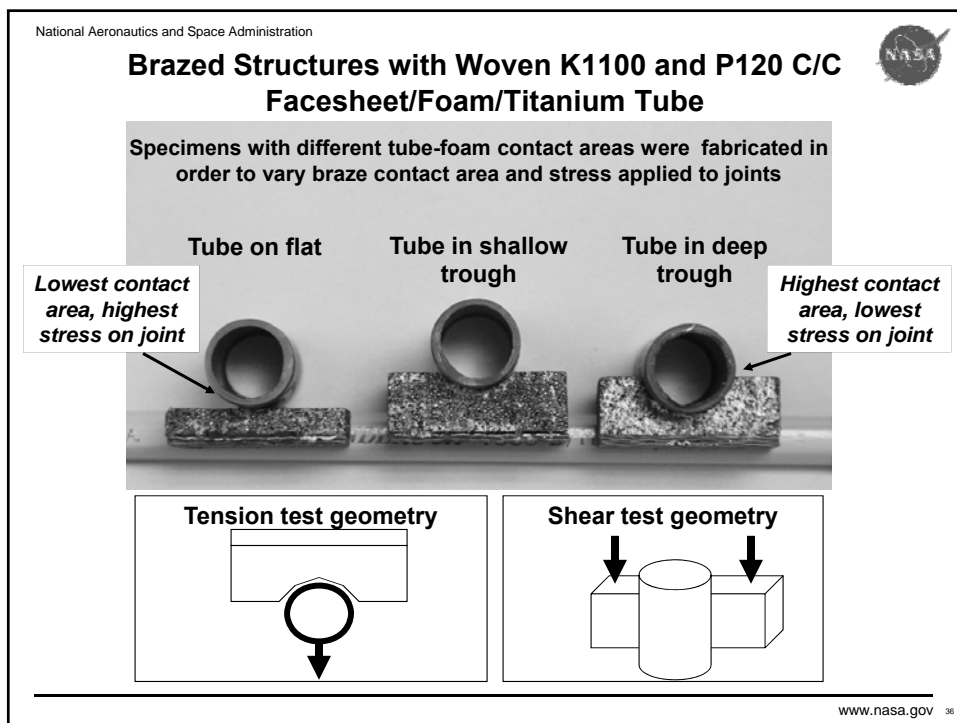
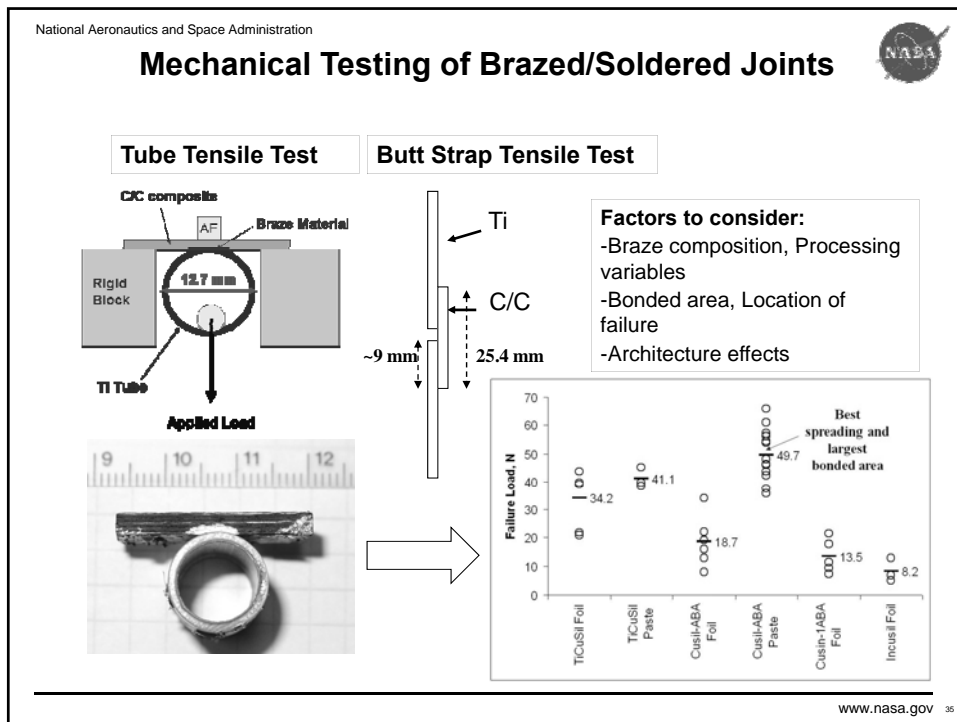


Large difference in CTE of C-C and metals lead to large residual stresses



$$\Delta\alpha = \alpha(\text{Ti}) - \alpha(\text{C/C})$$

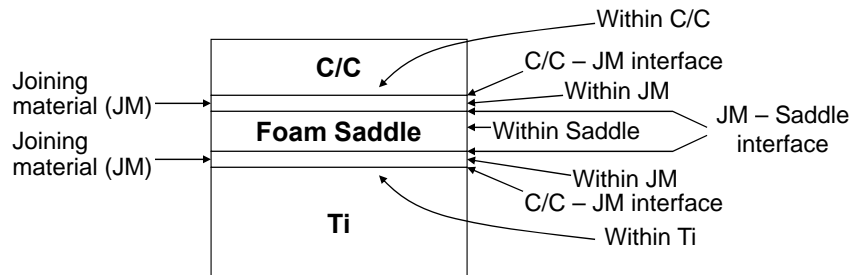
$$\Delta T = T(\text{liquidus} \sim \text{processing}) - 25^\circ\text{C}$$



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Locations of Potential Joint Failure in C/C Face Sheet/Poco Foam Saddle/Titanium



In addition the geometry of joining surfaces will affect strength of joint and influence spreading of joint material: flat to flat, flat to tube, curved surfaces...

Therefore, knowing the location of joint failure is critical

- **Weakest link requiring further improvement**
- **Affects interpretation of results (material or test-dependent property)**

Key factor: Bonded area dictated by braze composition and applied pressure, C/C constituent composition, fiber orientation, geometry of joined surface

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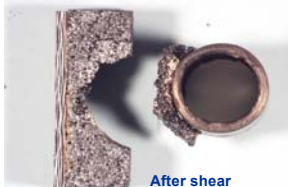


Brazed Structures with Woven K1100 and P120 C/C Facesheet/Foam/Titanium Tube

- Excellent bonding of CuSil-ABA Braze to Poco HTC, C-C Composite, and Ti Tube
- Failure always occurred in Poco HTC (Saddle Materials)



After Tension



After shear

Observations:

- The Poco HTC (carbon foam saddle material) is the weak link in the sandwich structures and not the brazed joint.
- Failure in tension and shear always occurs in the foam regardless of (1) P120 or K1100 woven face sheet materials or (2) whether the Ti tube was brazed to a curved Poco surface to maximize bond area or a flat Poco surface to maximize stress in the joint.
 - Maximum shear stresses subjected to braze exceeded 12 MPa based on load applied and approximate braze area.
 - Maximum tensile stresses subjected to braze exceeded 7 MPa based on load applied and approximate braze area.

M. Singh, G. Morscher, R. Asthana, T. Shpargel, *Mater. Sci. Eng., A* 498, 1-2 (2008) 31-36.

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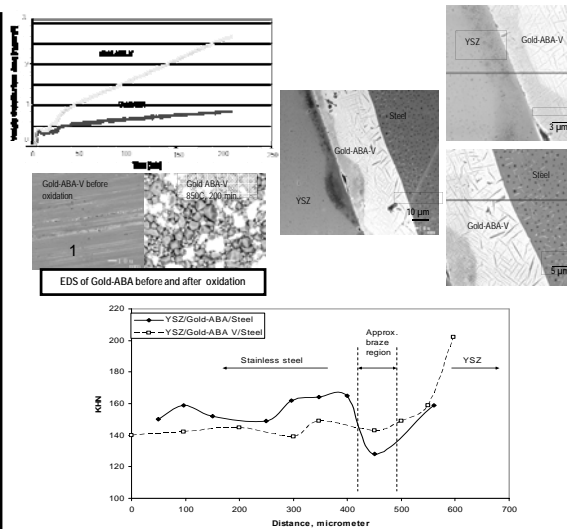


Ceramic Integration Technologies for Alternative Energy Systems - Solid Oxide Fuel Cells

Integration of YSZ/Steel for SOFC Applications



- Gold-ABA and Gold ABA-V exhibit linear oxidation kinetics at 850 C. Gold-ABA-V shows faster oxidation kinetics than Gold-ABA.
- Ti in Gold-ABA and V in Gold-ABA V caused discoloration (darkening) of YSZ.
- The darkening is caused by Ti and V that act as oxygen getters and form oxygen-deficient YSZ. No reaction layers formed at joint.
- The oxygen-deficient YSZ is better wet by gold than stoichiometric YSZ.



M. Singh, T. Shpargel, R. Asthana, Int. J. Appl. Ceram. Tech.
4(2), 2007, 119-133.



Integration of YSZ/Steel for SOFC Applications

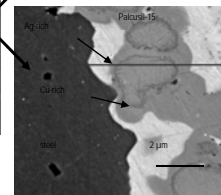
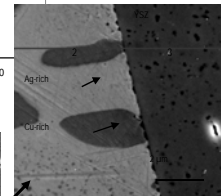
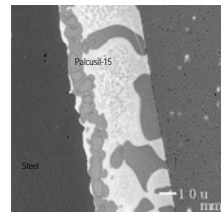
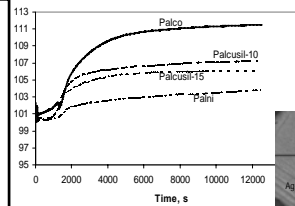
• Pd-base brazes (Palco and Palni) and Ag-base brazes (Palcusil-10 and Palcusil-15) were characterized for oxidation at 750°C.

• Structural changes accompany oxidation which is fastest for Palco, slowest for Palni, and intermediate for Palcusil-10 and Palcusil-15.

• All brazes were effective in joining yttria stabilized zirconia (YSZ) to stainless steel for solid oxide fuel cell (SOFC).

• Dissolution of YSZ and steel in braze, and braze constituents in YSZ and steel led to diffusion and metallurgically sound joints.

• Knoop hardness (HK) profiles are similar for all brazes, and exhibit a sharp discontinuity at the YSZ/braze interface.

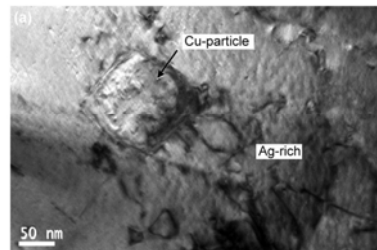


M. Singh, T. Shpargel, R. Asthana, *Mater. Sci. Eng. A* 485 (2008) 695-702.

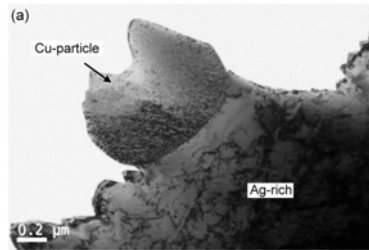
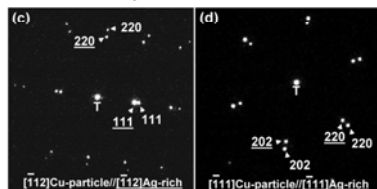
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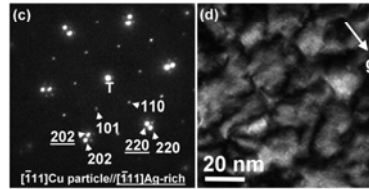
Transmission Electron Microscopy of Interfaces in YSZ/Ag-Cu-Pd/Steel System



(b) Atomic %	Ag	Cu	Fe	Cr	Pd	Zr
Cu-particle	3.8	79.8	2.2	1.5	9.8	2.9
Ag-rich	72.6	14.7	6.0	2.1	x	4.6



(b) Atomic %	Ag	Cu	Fe	Cr	Pd	Zr
Cu-particle	2.8	72.5	3.4	1.3	19.0	1.0
Ag-rich	81.9	7.9	4.1	1.5	2.5	2.1



K. Lin, M. Singh, and R. Asthana, Unpublished work (2010).

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Concluding Remarks

- **Ceramic integration technologies are critically needed for the successful development and applications of ceramic components in a wide variety of energy and aerospace applications.**
- **Significant efforts are needed in developing joint design methodologies, understanding the size effects, and thermomechanical performance of integrated systems in service environments.**
- **Global efforts on standardization of integrated ceramic testing are required. In addition, development of life prediction models for integrated components is also needed.**
- **There have been a number of short term design, development, and evaluation efforts in various parts of the world. However, a concerted and long term sustained effort is needed to make the significant progress in this area.**



Acknowledgements

- **Professor Rajiv Asthana, University of Wisconsin-Stout**
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- **Prof. J.M. Fernandez, University of Seville, Spain**
- **Dr. Gregory N. Morscher, University of Akron**
- **Mr. Ron Phillips, ASRC Corp.**
- **Mr. Ray Babuder, Case Western Reserve University**